

# **Conversion of Water to Hydrate Particles – Theory and Application**

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## **Abstract**

Natural gas hydrate is the single most important problem facing the oil and gas industry as it moves steadily towards deeper water. There is also a growing understanding in the oil and gas industry that hydrate particles are not necessarily a problem per se. If the particles do not deposit on walls or equipment, they may flow with the rest of the fluids and not create a problem.

CONWHYP — conversion of water to hydrate particles — is a novel concept developed by SINTEF with the aim of achieving conversion of free water to flowable “inert” hydrate particles, an end to hydrate plugging problems, better hydrate and corrosion control with less (or without) chemical additives, and improved environmental performance for offshore hydrocarbon production. Our process ensures that hydrate particles grow outwards from a starting nucleus, eliminating free water.

SINTEF have developed and tested a reactor aimed at achieving this goal in subsea settings close to a wellhead, and have been able to verify a method of producing “dry” hydrate particles without excess water, using only a specialized flow geometry. The work is now moving into its detailed design and engineering phase, and will progress towards full-scale testing in the future.

**Key words:** Natural gas hydrate, hydrate plugging, hydrate transport, crystal growth

## **Introduction**

The development of offshore mature basins is increasingly characterised by deepwater reservoirs. Feasible economic development of these reservoirs favours total subsea production systems without fixed or floating production platforms. A main issue for total subsea production systems is hydrate control.

Common to all hydrates is that water molecules, due to hydrogen bonding, form a three dimensional lattice whose voids are occupied by non-polar molecules with low molecular weight. At deepwater conditions thermodynamically stable hydrates will form if hydrocarbon fluids are cooled down to ambient temperature. Uncontrolled formation of hydrates may result in plugging of process equipment and transport pipelines.

Subsea transportation of unprocessed or minimum processed well fluids at low temperatures requires the use of large amounts of methanol or glycols for hydrate inhibition. In recent years new chemical additives have been developed to be effective at low concentrations. These additives act as hydrate kinetic inhibitors (Lederhos et. al.[1]) or as dispersants (Klomp et. al.[2]). A dispersant works by converting free water in a pipeline to dry powder hydrates without any hydrate deposits on the pipe wall, or highly viscous bulk intermediates. Even used at low concentrations these chemicals may be costly. Some of the most effective chemicals are also environmentally unfavourable.

In this paper a hypothesis and a concept for conversion of free water to flowable “inert” hydrate particles without use of any added chemicals are presented.

The formation of hydrate is in practice limited to the macroscopic interface between the water and hydrocarbon phases. After covering the interface with a hydrate phase, further growth depends on penetration of water or guest species across the hydrate phase. This process is still not well known, but an essential parameter is how hydrophilic hydrate surfaces are. Lund et. al. [3] have assumed that a hydrate film is solid and that water penetrates towards the hydrate-former-phase through small cracks due to capillary pressure made by the hydrophilic hydrate crystal surface. Sugaya and Mori [4] and Mori and Mochizuki [5] have assumed a similar process where water penetrates through distributed microperforations in the hydrate film. In an attempt to find how liquids wet hydrates Hirata and Mori [6] wetted a tetrahydrofuran hydrate rod with water. Their experiments indicated that clathrate hydrates have a highly

hydrophilic surface. In the absence of any liquid water they also found that even hydrophobic liquids might contact the hydrate surfaces at small contact angles.

Wolden [7] tested wetting with pure water, a 3.5 wt% NaCl solution, a 25 wt% methanol solution, pure methanol, and Exxsol D80 (paraffin cut) on tetrahydrofuran hydrates. The experiments were carried out by adding a droplet of the liquid to a horizontal steel plate covered by a porous tetrahydrofuran film. All liquids were found to wet the hydrate film with small contact angles. The spreading rate of the droplets on the hydrate film increased with the decrease of the surface tension of the liquids, with methanol and Exxsol D80 being the fastest. All liquids except Exxsol D80 (hydrophobic) penetrated the pores in the hydrate film indicating the hydrate surface to be hydrophilic. When a water droplet was added to a hydrate surface covered with an Exxsol D80 film, the water penetrated the Exxsol D80 film and spread on the hydrate film at a rate higher than without the Exxsol D80 film.

The following hypothesis may give some explanations for the macroscopic behaviour of hydrate formation observed in water, gas, and oil/condensate systems.

### **Conversion of gas bubbles to hydrates in water systems**

At hydrate formation conditions the first hydrate crystals will appear randomly on the bubble surface in the form of discrete particles, growing to enclose the bubble with a hydrate film (Figure 1). Once the bubble is completely covered with the hydrate layer the rate of reaction slows down (Maini and Bishnoi [8]). Further growth of the hydrate layer now takes place by water penetrating through distributed microperforations and small cracks in the hydrate film. The penetration is due to capillary pressure made by the hydrophilic hydrate surface against the gas phase. The cracks in the hydrate film are mainly formed by shrinkage of the bubble due to gas consumption by the hydrate formation. If the water phase outside the bubble is nearly stationary the growing rate is reduced as the hydrate layer increases in thickness as observed by Sugaya and Mori [4] and Brewer et. al [9].

If the surrounding water is imposing a hydrodynamic shear to a hydrate-coated bubble, particles or flakes of hydrates shedding from the bubble has been reported by Maini and Bishnoi [8], Topham [10] and Nojima and Mori [11]. The rate and thickness of hydrates shedding from a bubble was by Maini and Bishnoi [8] reported to increase with pressure. The shear forces to a hydrate layer around a bubble will create larger cracks in the layer as illustrated in Figure 2. Water flowing through these cracks will be wetting the hydrate surface by forming a water film on the hydrate layer. On top of this water film a new hydrate layer develops, leaving the old hydrate layer totally surrounded by water. The old hydrate layer is thereby free in the water phase and sheds off the bubble as particles or flakes due to the shear forces (Figure 2). The rate of this process increases with the driving force for hydrate formation and shear forces to the bubbles. If the water phase is saturated with the hydrate forming species, the hydrate flakes and particles produced in this way are stable. Andersson [12] produced up to 21 vol% hydrate in water slurries from bubbles of methane and a gas mixture. In all slurries the hydrates behaved like dry particles without any tendency to agglomerate or deposit on pipe walls. In a similar manner Lund et. al. [13] observed droplets of liquid HFC-13 in a closed water loop converting into to small dry hydrate flakes without any tendency of agglomeration or deposits to the pipe wall.

### **Conversion of a water droplet to hydrates in hydrocarbon gas or liquid systems**

Hydrates start to nucleate close to the hydrocarbon phase on a water droplet in a gas, oil, or condensate phases (Kvamme [14]). After stable nuclei are reached they grow along the surface of the droplet until it is completely covered with a thin hydrate layer. Water then penetrates from the interior of the water droplet to the hydrophilic hydrate surface against the hydrocarbon phase through microperforations or small cracks in the hydrate film as illustrated in Figure 3. The formation rate decreases as the hydrate layer increases in thickness, depending on the hydrate formation driving force and shear forces to the droplets. Sugaya and Mori [4] found the hydrate film on a stagnant HFC-

134a-water planar interface conserved at a thickness of about 10  $\mu\text{m}$  at 278.45 K and  $5.8 \cdot 10^5$  Pa. Seleznev and Stupin [15] sprayed water droplets into a vessel with methane gas at 263 K and  $4 \cdot 10^6$  Pa to  $1.2 \cdot 10^7$  Pa. They found that 15% of the water in the droplets converted to hydrates in  $\leq 0.2$  seconds. After this time no further conversion of water (ice) to hydrates was observed during the experiments.

If a water droplet covered by a hydrate film hits e.g. a pipe or reactor wall in a turbulent system, the kinetic force of the droplet will create larger cracks in the film. Free subcooled water inside the droplet will drain through these cracks and spread on the hydrophilic hydrate film as illustrated in Figure 4. Hydrate forming species on the pipe wall may convert this water to hydrate at a fast rate, often resulting in deposition of the droplet on the wall.

### **Conversion of water to hydrates in turbulent hydrocarbon liquid systems**

The macroscopic development of water converting to hydrates in turbulent oil or condensate systems may vary with the system. However, based on experimental studies (Aalvik [16], Fauskanger [17], Løken [18], Austvik [19,20], Lund [13,21,22]) there seems to be some basic elements in the conversion process where any deviations may be explained by system parameters and fluid compositions.

In turbulent liquid systems the water phase is often distributed in the hydrocarbon phase as rough unstable water in oil emulsions. At initiation the hydrates start to grow on the water-hydrocarbon interface covering the droplet with a thin hydrate layer. As surface tension of the droplets increases due to the hydrate layer, the water droplets agglomerate to larger droplets or water lumps in order to decrease surface areas as shown in Figure 5.

In turbulent liquids the water lumps will change form, surface area, and volume continuously. The thin hydrate layer on the water lump will thereby often be broken giving new free water-hydrocarbon interfaces where more hydrates quickly form. The

turbulent forces will also create small hydrate covered water droplets as illustrated in Figure 6. Due to the hydrophilic properties of a hydrate surface these droplets will be absorbed in the water lumps making a slurry like appearance (Aalvik [16]).

With time, the hydrate film on the water lumps grows thicker. When turbulent forces make cracks in this film, free water may be drained from inside the water lump and spread on the hydrophilic hydrate layer towards the hydrocarbon phase. New hydrates may form on top of this water leaving bits of the old hydrate layer totally surrounded by free water (Figure 7). These particles disperse in the water phase giving it a white appearance.

The number of hydrate particles inside the water/hydrate lump increases until forces between the hydrate particles make the outer area of the lump stiffer. When these lumps collide with each other or with e.g. a pipe wall, free water from the lump interior will spread to the outer hydrate surface acting as “glue” for agglomeration of the lumps to bigger lumps or plugs (Figure 8) or to the pipe wall by converting to hydrates. According to Austvik [20] about 30% of free water may be converted to hydrates at this stage.

Water may continue to convert to hydrates by transportation of free water from the interior of the water/hydrate lumps or plugs by capillary forces through cracks and microperforations in the outer hydrate layer (Figure 9). The hydrate layer covering lumps or plugs increases in thickness until internal pressure gradients due to capillary forces breaks them down to smaller hydrate bits as illustrated in Figure 10. This process continues until the lumps have been broken down to a powder like appearance. However, the “hydrate powder” may still contain enclosed up to 30 % free water (Austvik [20]), causing deposits to e.g. a pipe wall later (Lund [22]).

### **A new concept for producing dry hydrates in oil or condensate well streams**

If water is to be transported as a more or less dilute hydrate slurry in a pipeline from a subsea oil or condensate field, the hydrates must contain no free water in order to

avoid any problems from deposits on the pipe wall or agglomeration at stop or start of the pipeline flow. In order to achieve this, free water from a subsea well will have to be converted to hydrates near the well in a fast and controlled manner without any deposition-prone intermediate stages. In the following conceptual description this is done without chemical additives by using the fact that hydrate surfaces exhibit a high degree of hydrophilic behaviour.

If a warm oil or condensate well stream containing free water droplets is mixed with a cooled well stream containing a large number of dry hydrate particles, the water will quickly coat the hydrate particles with a thin water film. By further cooling of the mixture, the water will be converted to hydrates by growing from the existing hydrate surfaces and outwards. This should ensure that no free water is encapsulated within the hydrate particles, and therefore no later agglomeration or deposition can take place.

This process is the subject of a patent application [23] involving the authors and colleagues from SINTEF – a Norwegian contract research organization. Testing and validation of the hypotheses is ongoing in an industry-sponsored project named CONWHYP – conversion of water to hydrate particles. The overall objective for the CONWHYP project is to achieve:

- conversion of free water to flowable “inert” hydrate particles, and
- an end to hydrate plugging problems, and
- better hydrate and corrosion control with less (or without) chemical additives, and
- improved environmental performance for offshore hydrocarbon production.
- pipeline transport in thermal equilibrium with the surroundings

This will be achieved through development of a simple and effective "hydrate reactor" for instalment close to a wellhead or pipeline starting point. The concept is developed with liquid-dominated systems in mind, but variations are also studied for gas-rich applications.

Figure 11 gives a schematic overview of the processes described in the following. At the start of the pipeline, either sub-sea, or onboard a minimum processing



platform, or conceivably downhole in individual production wells, water separation is efficient enough that after cooling and condensation, no more than a certain amount of water is present in the fluid stream.

Afterwards, the fluids are cooled rapidly towards hydrate stability temperatures in exposed (uninsulated) pipes of the necessary length. The phases may also be mixed, to provide a large interfacial surface area. Upon entering the hydrate reactor part of the system (which may be nothing more than a section of pipe) hydrate particles and a cold fluid stream are mixed in from a downstream split. Water wetting of the hydrate particles will take place, and hydrate growth will be from the existing particle surfaces and outwards. The hydrate formation process is thus aided by the addition of cold fluid (inside the hydrate stability pressure-temperature region), and - most importantly - the already present hydrate particles. Further cooling takes place through the reactor.

All of the water in the stream shall be converted to dry hydrate particles by the time it reaches the end of the reactor. Then it enters a very simple separator (or just a flow-splitter), where some of the cold hydrocarbon fluids and dry hydrate particles are taken out, and re-injected at the reactor inlet, as described above.

The particles escaping without being recirculated will be solid, dry hydrate. The aim for the separation, or flow-splitting process is to have some of the fully converted particles proceed downstream, in an amount corresponding to the content of water in the inflow to the reactor. The additional cooling in the hydrate reactor will have brought the system close to ambient temperature, and this will prevent further condensation of water from either liquid or gas hydrocarbon phases through the rest of the pipeline.

The hydrate powder will not melt back to free the water and natural gas until temperatures rise or pressures become too low - which will be at the end of the transport, where the process will not be problematic. The powder can be mechanically separated from the bulk liquid phase by a sieve (unlike dispersant-induced emulsions which are often difficult to break). Depending on the fluid system, the particle density

may even be different enough from the bulk liquid that the particles may easily be drained from the bottom of the separator tank.

### **Environmental considerations**

This concept is expected to contribute considerable positive environmental effects. The development of a safe and efficient way to transport free water in the form of hydrate particles will dramatically reduce the need for a host of different chemical additives which are used today, both hydrate and corrosion inhibitors. This will impact all aspects of the hydrocarbon production process, from working conditions on production and processing facilities, to the effect on the ecosystem through leaks, accidental discharges or injection system malfunctioning.

A secondary, but no less important, environmental effect will be the improved safety aspects in pipeline operation: with the hydrate plugging and corrosion risks minimised, the danger of pipeline ruptures and large-scale blowouts will also be lowered. This is in addition to the fact that a cold fluid stream without temperature-induced changes in the fluid composition and properties makes the whole pipeline a more well-defined system to operate.

### **Experimental equipment**

Since mid-1999, the CONWHYP concept has been the object of experimental testing, in a circulation loop built at the SINTEF laboratories in Norway. The loop was built from stainless steel, and is normally operated at close to  $7 \cdot 10^6$  Pa during experiments. Figure 12 shows a detailed sketch of the actual loop, and a schematic representation of the surrounding equipment.

The reactor part of the loop (a 0.1 m diameter section) and the closest connected pieces are internally coated with Teflon to avoid deposition in these areas. The flow in the loop is driven by a propeller connected through a magnetic coupling to an outside motor. To date, the results and conclusions from the experiments are based mainly on

visual observations during experiments, as well as temperature, pressure and flow conditions.

## **Experiments**

Several long-time experiments (i.e. running at experimental conditions for 10 hrs. or more) were performed. A typical experiment consisted of cooling the entire laboratory, pressurizing the loop with oil, and then injecting methane and propane in specified amounts. The hydrate equilibrium conditions for the usual mixture are shown in Figure 13. The subcooling below equilibrium at operating conditions was greater than 12 K. Water was then injected at carefully controlled rates. Evolution of the water droplets to hydrate particles, and their deposition and agglomeration characteristics were studied by visual observation. The exact results of the experiments are currently confidential, and will be reported in detail at a later time.

## **Concept validation**

For a practical implementation, some special means of hydrate initiation may be needed for the very first startup situation to make the initial mass of hydrate particles, but thereafter any shut-in of the pipeline should be able to conserve enough dry hydrate particles in the recirculation loop to be sufficient for a new startup. Thus the problem of creating a startup mass will be a once in the field lifetime process, after which it will be self-sustaining.

The major conclusion from the work so far, is that the basic principle – production of dry hydrate from water spreading on existing hydrate particles – seems to work as described earlier. This means that the actual implementation and exploitation of this concept in realistic situations is only a question of engineering challenges, and not of the involved physical mechanisms

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## References

- [1] J.P. Lederhos, J.P. Long, A. Sum, R.L. Christiansen and E. D. Jr. Sloan, Chem. Engng. Sci., 51 (1996) 1221-1229.
- [2] U.C. Klomp, V.R. Kruka, R. Reijnhart and A.J. Weisenborn, A Method for Inhibiting the Plugging of Conduits by Gas Hydrates, 1995, Patent WO 95/17579.
- [3] A. Lund, O. Urdahl, O. Lier, L.H. Gjertsen, T. Jakobsen and J.A. Støvneng, Proc. 7th Int. Offshore and Polar Eng. Conf., Honolulu, USA, May 25-30, 1997, p. 110.
- [4] M. Sugaya and Y.H. Mori, Chem. Eng. Sci., 51 (1996) 3505-3517.
- [5] Y.H. Mori and T. Mochizuki, Chem. Eng. Sci., 52 (1997) 3613-3616.
- [6] A. Hirata and Y.O. Mori, Chem. Eng. Sci., 53 (1998) 2641-2643.
- [7] M. Wolden, Diploma Thesis, Dep. Refrigeration and Air Conditioning, The Norwegian Univ. of Sci. and Technology, Trondheim, Norway, 1998.
- [8] B.B. Maini and P.R. Bishnoi, Chem. Eng. Sci., 36 (1981) 183-189.
- [9] P.G. Brewer, M.O.Jr. Franklin, G. Friederich, K. A. Kvenvolden, D.L. Orange, J. McFarlane and W. Kirkwood, Geology, 25 (1997) 407-410.
- [10] D.R. Topham, Chem. Eng. Sci., 39 (1984) 821-828.
- [11] K. Nojima and Y.H. Mori, Proc. 10th Int. Heat Transfer Conf., Rugby, U.K., 3 (1994), 377-382

- [12] V. Anderson, Dr.ing. Thesis, Dep. of Petrol. Eng. and Appl. Geophysics, The Norwegian Univ. of Sci. and Technology, Trondheim, Norway, 1999.
- [13] A. Lund, D. Lysne, Ø. Grande and T. Austvik, SINTEF Report STF21 A92034 (1992), Trondheim, Norway.
- [14] B. Kvamme, Proc. 2<sup>nd</sup> Int. Conf. Nat. Gas Hydrates, Toulouse, France, June 2-6, 1996, p. 139.
- [15] A.P. Seleznev and D.Yu. Stupin, Kolloid Zh., 39 (1977) 86-91.
- [16] J. Aalvik, Diploma Thesis, Dep. of Refrigeration Eng., The Norwegian Univ. of Sci. and Technology, Trondheim, Norway, 1987.
- [17] R.F. Fauskanger, Diploma Thesis, Dep. of Chem. Eng., The Norwegian Univ. of Sci. and Technology, Trondheim, Norway, 1988.
- [18] K.-P. Løken, Diploma Thesis, Dep. of Chem. Eng., The Norwegian Univ. of Sci. and Technology, Trondheim, Norway, 1989.
- [19] T. Austvik, A. Lund, D. Lysne, E. Lindeberg and K.-P. Løken, SINTEF Report STF21 A90006 (1990), Trondheim, Norway
- [20] T. Austvik, Dr.ing. Thesis, Division of Thermodynamics, The Norwegian Univ. of Sci. and Technology, Trondheim, Norway, 1992.
- [21] A. Lund, D. Lysne, T. Austvik and B. A. Ardø, SINTEF Report STF21 A91040 (1991), Trondheim, Norway.
- [22] A. Lund, D. Lysne, SINTEF Report STF21 A92073 (1992), Trondheim, Norway
- [23] A. Lund, D. Lysne, R. Larsen, and K.W. Hjarbo, *Method and system for transporting a flow of fluid hydrocarbons containing water*, patent application PCT/NO99/00293

## Figure captions

- Figure 1* Growing of a hydrate film on a gas bubble in water.
- Figure 2* Shedding of hydrate particles from a gas bubble exposed to shear forces in water.
- Figure 3* Growth of hydrate layer on a water droplet surrounded by hydrocarbons.
- Figure 4* Hydrate-covered droplet hitting a surface.
- Figure 5* Agglomeration of water droplets after hydrate initiation.
- Figure 6* Hydrate-covered water droplets inside larger water lumps. The start of slurry-like flow behaviour.
- Figure 7* Hydrophilic interaction causing water spreading and inclusion of hydrate particles.
- Figure 8* Agglomeration of water/hydrate lumps and deposition caused by availability of free water.
- Figure 9* Ongoing conversion of water to hydrate by water transport to surface of large lumps.
- Figure 10* Breakup of large hydrate lumps.
- Figure 11* Schematic description of the hydrate reactor concept. See text for details.
- Figure 12* Schematic representation of the flowloop and surrounding equipment.
- Figure 13* Calculated hydrate dissociation curve for our typical fluid composition.

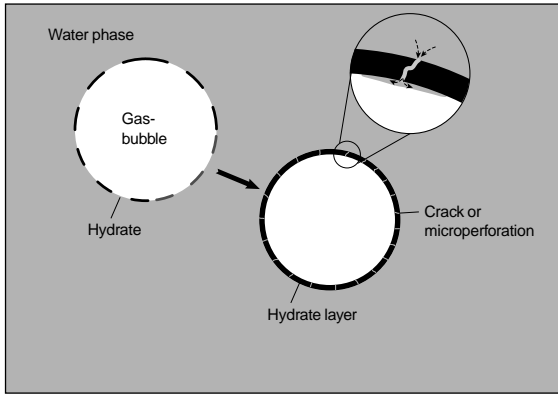


Figure 1

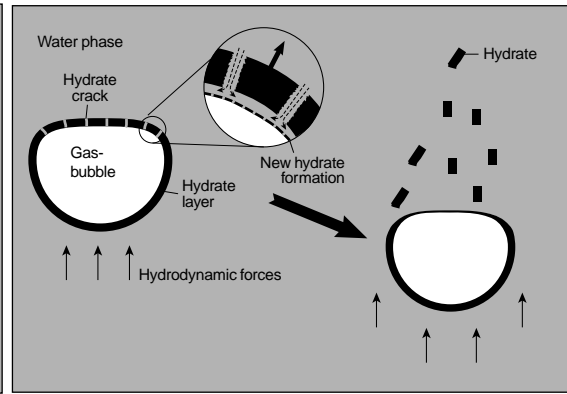


Figure 2

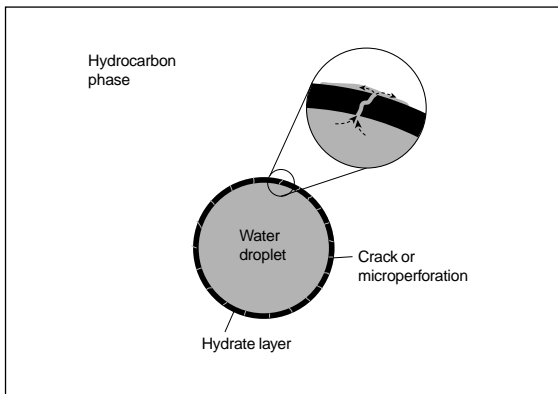


Figure 3

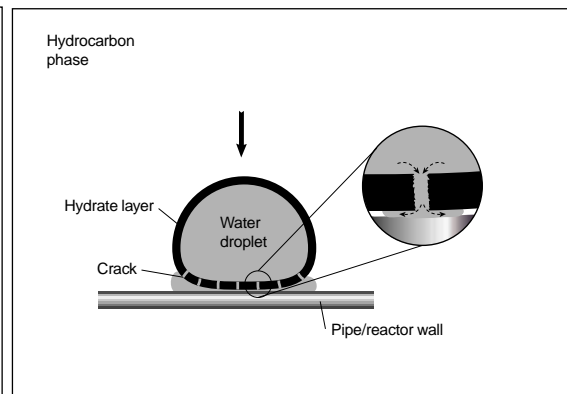


Figure 4

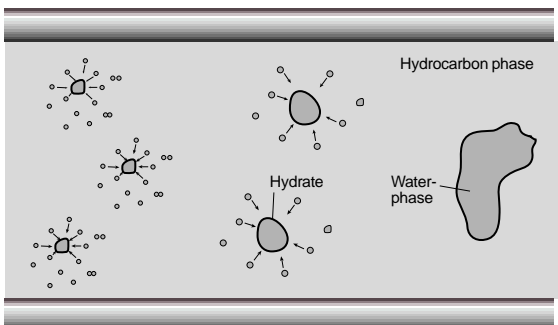


Figure 5

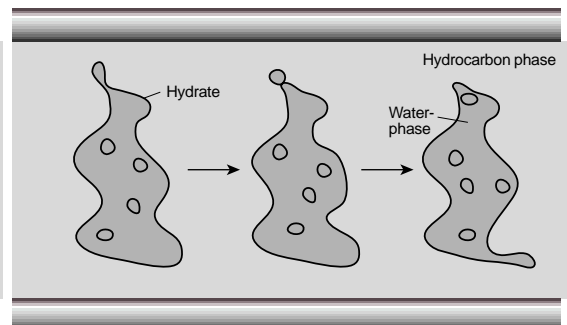


Figure 6

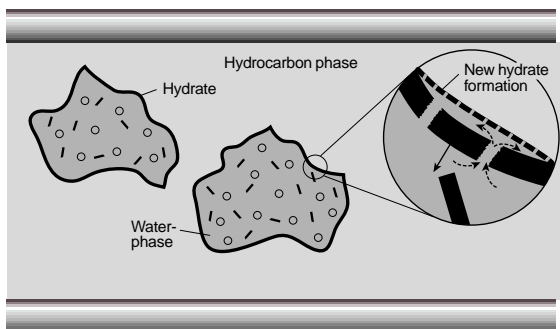


Figure 7

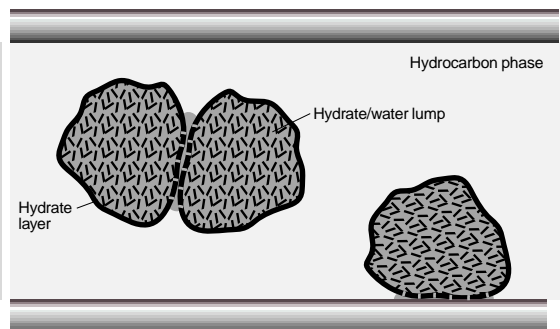


Figure 8

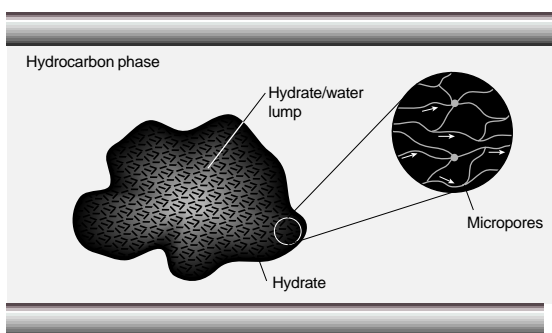


Figure 9

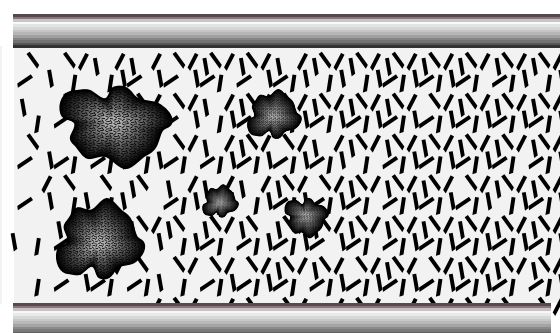


Figure 10

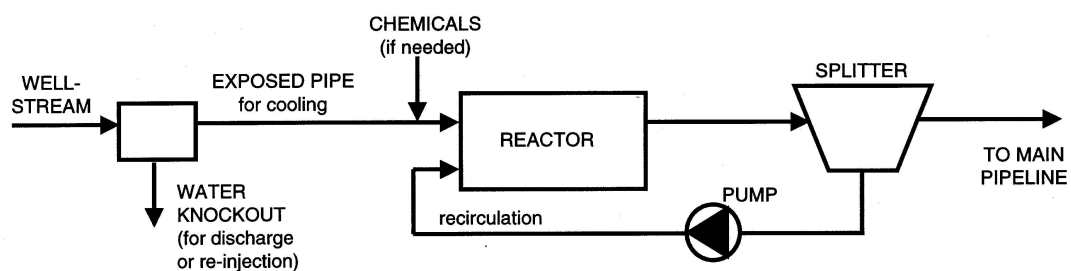


Figure 11



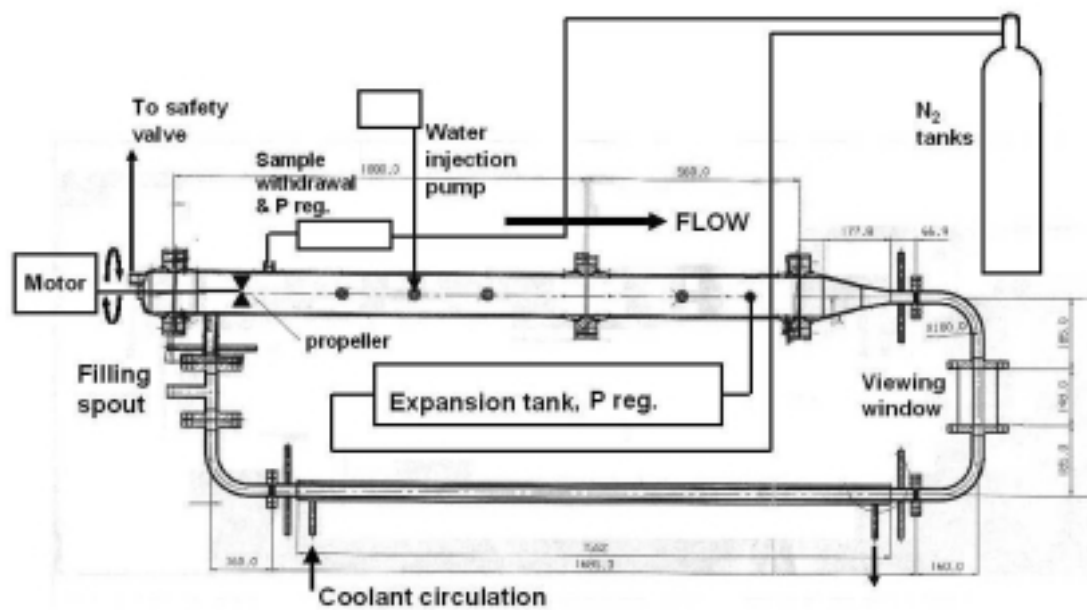


Figure 12

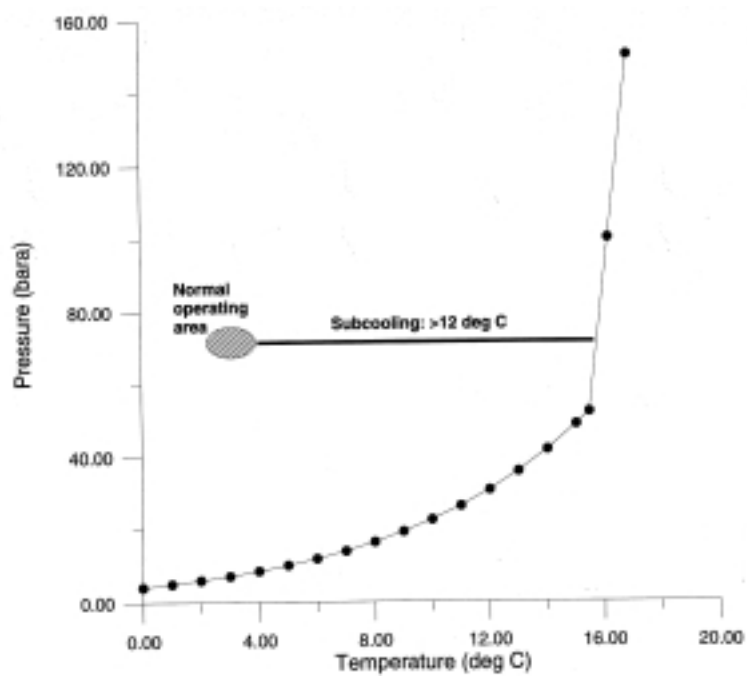


Figure 13